

ON THE DETERMINATION OF THE VAPOR-LIQUID ENVELOPE FOR POLARIZABLE MODELS BY MONTE CARLO SIMULATION

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ABSTRACT

We present Gibbs Ensemble Monte Carlo simulations of SCPDP polarizable model for water. Our results agree well with the literature data and seem to be more accurate for the vapor phase. Our simulations suggest that Gibbs Ensemble Monte Carlo of polarizable models with exact treatment of the polarizable interactions is feasible, though its efficiency is rather low. Application of a newly proposed approximate method to treat the polarizable interactions in Monte Carlo is expected to remedy this deficiency.

INTRODUCTION

One of the most important features of water and aqueous solutions is the presence of sizeable polarization effects. These multibody effects are responsible for the approximately 1.0 D enhancement of the water dipole moment at ambient conditions over that of the isolated monomer (1.85 D). Traditionally, this enhancement has been described in terms of pairwise electrostatic interactions with enhanced fixed charges, usually considered as adjustable parameters, and resulting in permanent dipole moments between 2.12-2.35 D. These nonpolarizable models, such as SPC, SPC/E, and TIP4P, have been rather successful in mimicking the behavior of water at the conditions of parameterization, and not surprisingly, at conditions for which the actual dipole moment of water is of similar size as that of the model ¹. However, these polarization effects at gas-like supercritical conditions are likely to be less important, and therefore, the resulting effective dipole moment should be closer to its gas-phase value. Thus, we expect the above models to overpredict the polarization effects, while models obtained by simply rescaling the point charges to yield dipole moments closer to 1.85 D might significantly improve (over the corresponding original models) the description of the microstructure of water at near and supercritical conditions ².

In principle, this scenario indicates the need for polarizable interactions to account explicitly for the multibody response to environmental changes, and therefore, to be able to describe satisfactorily water properties over a wide range of state conditions. In practice, at the present time, this does not seem to be the case ^{3,4}, most probably, due to inappropriate

parameterization of current polarizable models. The goal of developing a polarizable model for water which yields an accurate phase envelope remains elusive and will continue to be until we can routinely and efficiently predict the phase envelope of polarizable fluids.

Only a few attempts have been done in the determination of the phase envelope of polarizable models, including Kiyohara *et al.* ⁵ grand canonical Monte Carlo simulations of water using a histogram reweighting technique, Medeiros & Costas' ⁶ Gibbs ensemble Monte Carlo (GEMC) simulation of the TIP4P-FQ fluctuating charge model ⁷, Yezdimer & Cummings' Gibbs-Duhem simulations of the latter model ⁸, and the latest GEMC simulations of the same model by Chen *et al.* ^{9,10}. The simulation of polarizable models by Monte Carlo (MC) suffers from an inherent problem not found in its molecular simulation (MD) counterpart. While all pair interactions of N molecules are evaluated every integration time step in MD, and the polarization interaction requires little additional CPU-time, the electronic configuration of N molecules must be updated after each single MC move of a molecule. This feature makes the MC simulation of polarizable models N -times slower than the MC of non-polarizable models, and consequently, making it very inefficient for the determination of coexistence lines for polarizable model fluids.

Some effort has been placed on developing ways to reduce the need for the N^2 interaction calculations in the MC simulation of polarizable fluids, such as the so-called *single molecule update* approach (and variations) used by Medeiros & Costas ⁶ and Martin & Siepmann ¹¹. However, at least for the models with induced dipole moments, we have recently shown ¹² that these methods introduce an unacceptably biased sampling, even for NVT simulations. Our ultimate goal is to apply the new *Pair Approximation for*

Polarization Interaction (PAPI), which proved to be quite promising in our *NVT*–*MC* study ¹² and by far superior to the single molecule update method, to GEMC simulations. As a first step, here we present GEMC simulation results for the SCPDP water model ¹³ using the full iteration process (rather than any approximation) to check the applicability of GEMC method to polarizable models, and to assess the accuracy and computer time requirements of these simulations.

SCPDP WATER MODEL

The model consists of a rigid geometry of the SPC water model, *i.e.*, a planar configuration with an $H-O-H$ angle of 109.5° and an $O-H$ bond length of 1.0 \AA . The electrostatic charges are located on the H sites and at a distance R_{OM} toward the H sites along the $H-O-H$ bisector, with magnitudes such that the permanent dipole moment is that of the isolated water molecule, *i.e.*, 1.85 D. With this geometry, the model consists of a Lennard-Jones $O-O$ pair plus the electrostatic interactions from all charges. In addition, we include an isotropic linear point-dipole polarizability at the center of mass to account for the many-body polarizability effects. For a system of N water molecules, with s permanent charges and a point dipole polarizability, the induced dipole moment \mathbf{p}_i on the center of mass of molecule i is given by,

$$\begin{aligned}
\mathbf{p}_i &= \alpha \mathbf{E}_i \\
&= \alpha (\mathbf{E}_i^q + \mathbf{E}_i^p)
\end{aligned} \tag{1}$$

In equation (1) α is the scalar molecular polarizability, \mathbf{E}_i is the total electric field on the center of mass of molecule i whose contribution from the permanent charges of sites γ on molecule j is given by,

$$\mathbf{E}_i^q = \sum_{j \neq i}^N \sum_{\gamma=1}^s q_j^\gamma \frac{\mathbf{r}_{i,j\gamma}}{|\mathbf{r}_i - \mathbf{r}_{j\gamma}|^3} \tag{2}$$

while the corresponding polarization contribution at the center of mass of molecule i is given by,

$$\mathbf{E}_i^p = \sum_{j \neq i}^N \mathbf{T}_{ij} \cdot \mathbf{p}_j \tag{3}$$

In the preceding equations we used the following notation: $\mathbf{r}_{i\beta,j\gamma} = \mathbf{r}_{i\beta} - \mathbf{r}_{j\gamma}$, where $\mathbf{r}_{i\gamma} = \mathbf{r}_i + \mathbf{r}_i^\gamma$ and \mathbf{r}_i are the vector positions of site γ and center of mass of molecule i , respectively. In eq. (3) \mathbf{T}_{ij} is the symmetric dipole tensor,

$$\mathbf{T}_{ij} = \frac{1}{r_{ij}^3} \left(\frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} - \mathbf{I} \right) \quad (4)$$

and \mathbf{I} is the unit tensor.

The total electrostatic energy for this system is given by ¹⁴ ,

$$U = U_{qq} + U_{\text{pol}} \quad (5)$$

where the charge-charge contribution U_{qq} is given by,

$$U_{qq} = 0.5 \sum_{j \neq i}^N \sum_{\beta}^s q_i^{\beta} \mathbf{E}_i^q \quad (6)$$

and the polarization contribution U_{pol} by,

$$U_{\text{pol}} = -0.5 \sum_{i=1}^N \mathbf{p}_i \mathbf{E}_i^q \quad (7)$$

SIMULATION METHOD

We performed GEMC simulations with 341 SCPDP ($R_{OM}=0.1$ Å) water molecules at $T= 480$ K and $T= 510$ K, which has been already studied by Kiyohara *et al.* ⁵ using a series of grand canonical MC simulations in combination with histogram reweighting technique to obtain the coexistence state points. We used the standard GEMC technique, *i.e.*, both liquid and vapor boxes were simulated explicitly. The reaction field technique was used for long-range electrostatic interactions beyond the cutoff distance 8.5 Å. Since the acceptance of transfer of a molecule between the boxes is close to 1% at these high temperatures, the molecule transfer was attempted on average every 10 displacements. About 3 volume changes per MC cycle were performed.

In MC simulations, the change of a position of a molecule and especially the insertion of a new molecule can lead to a configuration with two molecules at very close separation. In such cases, the polarization catastrophe ¹⁴ leading to a divergence of energy can happen. To avoid this problem, which is artificial and arises from the lack of hard core repulsion in the potential, the trial displacements and insertions resulting in an intermolecular separation smaller than 2.3 Å were immediately rejected. The value 2.3 Å is large enough to prevent the polarization catastrophe, yet it does not affect the sampling, since the minimal intermolecular separation in all accepted configurations is always larger than 2.4 Å.

We treated the polarization interaction exactly, *i.e.*, by performing the full iteration, which requires the lengthy evaluation of dipole-dipole interactions between each pair of

molecules. The full iteration procedure calculates $N(N-1)/2$ interactions, where N is the number of molecules. The quadratic dependence on the number of molecules makes this step the slowest part of the simulation. The useful tricks, such as that of keeping all intermolecular distances and even the components of the polarization tensor T_{ij} in arrays can only minimize this disadvantage. The number of nonpolarizable pair interactions which are calculated during a MC step is proportional to $2(N-1)$, however the proportionality constant is about 10, if we consider 3 charged sites on a molecule plus a single Lennard-Jones site. Therefore, for the typical simulation system size (200-500 molecules), the full iterative procedure is 'only' by an order of magnitude slower than the nonpolarizable part of energy calculation and not N times, as it might be expected on the first sight.

PRELIMINARY RESULTS

The time evolution of the instantaneous coexistence densities is shown in Figures 1 and 2, while the average thermodynamic properties are shown in Tables 1 and 2. The agreement between our results and those from Kiyohara *et al.* ⁵ is quite good for liquid phase. However there is a discrepancy in the vapor phase at both temperatures. Our average energies are more negative and our densities are smaller than those reported in Ref. 5. To verify this point, we performed NVT simulations at the vapor conditions given by Kiyohara *et al.* For $\rho=0.036$ g/cc and $T=480$ K, we obtained an average configurational energy of

-3.4 ± 0.4 kJ/mol, while for $\rho=0.070$ g/cc and $T=510$ K, the average configurational energy was -5.7 ± 0.5 kJ/mol. Both results indicate that the reported data for the vapor phase are not consistent or less accurate. However, considering the rather different approaches used in these studies, the agreement between both kinds of simulations is fairly good.

The GEMC simulations are subject to considerable fluctuations, which restrict the accuracy of results. The fluctuations become larger when the increasing temperature approaches the critical point, as can be clearly seen by comparing Figures 1 and 2. The fluctuations are particularly clear from Figure 3, where the number of molecules in one of the boxes is shown. The coexistence pressures reported by Kiyohara *et al.* for $T=480$ K and $T=510$ K are 45 bar and 89 bar, respectively, in agreement with our values obtained in the vapor phase, *i.e.*, 56 ± 12 bar and 103 ± 21 bar. However, the corresponding liquid phase pressures could not be determined accurately due to persistent large fluctuations of about ± 400 bar.

FINAL REMARKS

Our illustrative example on the GEMC simulation of a polarizable water model suggests that the full iteration approach to equation (1) is feasible, though the evaluation of dipole-dipole interaction between all pairs every MC step slows down the simulation by a factor of 8-10 with respect to the nonpolarizable counterpart. The time required to simulate a thousand cycles was about an hour on a PC computer. As a result, this method is better

suited to a few benchmark simulations at selected thermodynamic points rather than to perform a series of simulations. Especially with increasing system sizes, the computer effort required on the exact full iterative procedure becomes prohibitive and an alternative more efficient method for performing MC simulations, including GEMC, is of particular interest. The PAPI method introduced recently by us appears promising. Its application to GEMC simulations, which is currently being developed, would increase considerably the efficiency of phase envelope determinations.

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TABLES:

	ρ_g [g/cc]	ρ_l [g/cc]	U_g [kJ/mol]	U_l kJ/mol]	μ_g [kJ/mol]	μ_l [kJ/mol]
GEMC	0.032(5)	0.73(3)	-3.1(8)	-26.8(10)	-29.0	-27.3
Ref. [5]	0.036	0.758	-2.5	-28.1		

Table 1: Average densities ρ , potential energies U , and chemical potentials μ of coexisting liquid and vapor phases of SCPDP model at temperature $T=480$ K. The numbers in parenthesis give the uncertainty of the last digit.

	ρ_g [g/cc]	ρ_l [g/cc]	U_g [kJ/mol]	U_l kJ/mol]	μ_g [kJ/mol]	μ_l [kJ/mol]
GEMC	0.063(6)	0.64(6)	-5.0(7)	-23.6(16)	-29.2	-27.4
Ref. [5]	0.070	0.640	-4.7	-24.2		

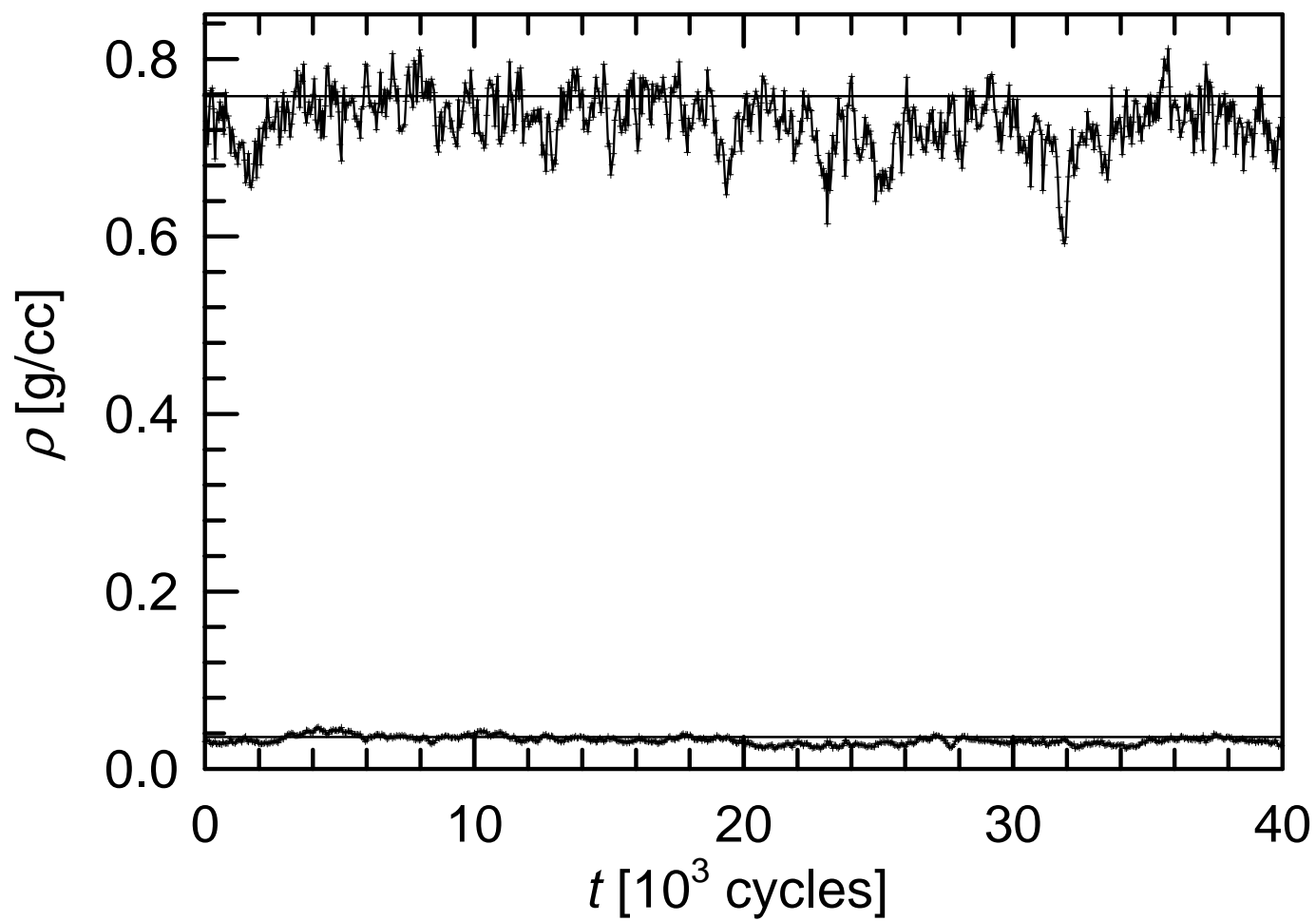
Table 2: Average densities ρ , potential energies U , and chemical potentials μ of coexisting liquid and vapor phases of SCPDP model at temperature $T=510$ K.

FIGURE CAPTIONS

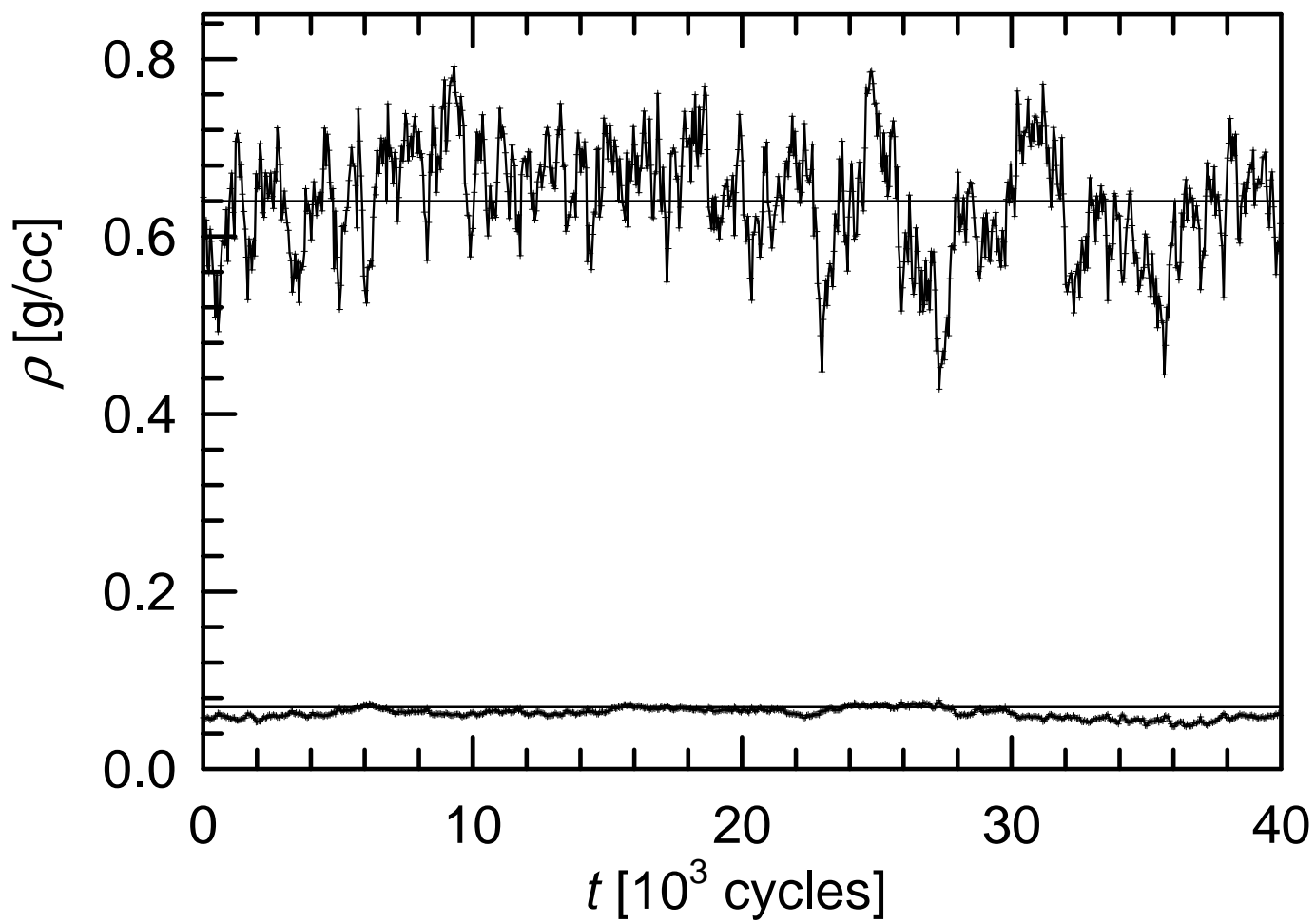
Fig. 1: Instantaneous densities for the liquid and vapor phases from the GEMC simulation of SCPDP water at $T=480$ K. The average densities given by Kiyohara *et al.* are shown as horizontal lines.

Fig. 2: Instantaneous densities for the liquid and vapor phases from GEMC simulation of SCPDP water at $T=510$ K. The average densities given by Kiyohara *et al.* are shown as horizontal lines.

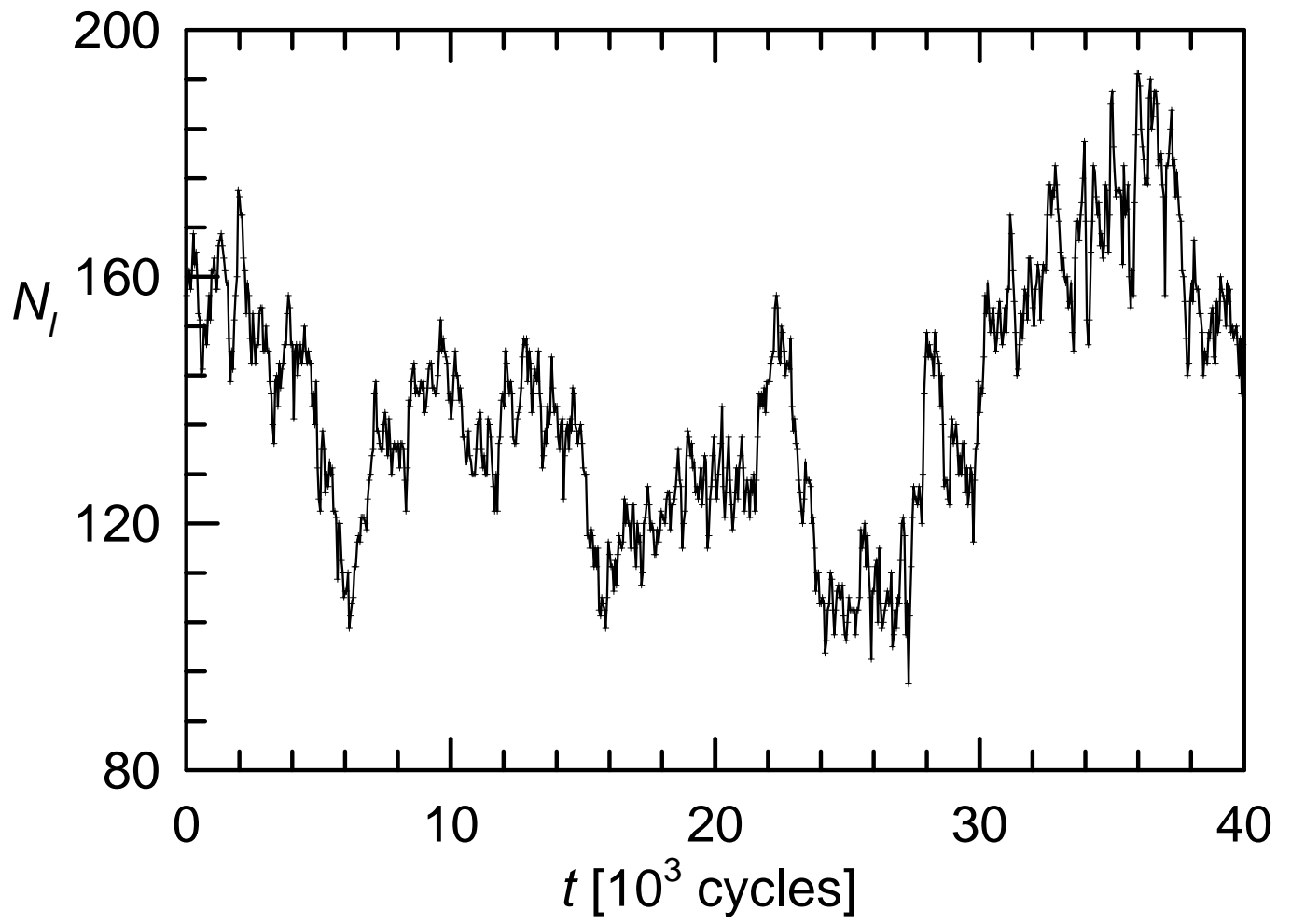
Fig. 3: Instantaneous number of molecules in the liquid phase from GEMC simulation of SCPDP water at $T=510$ K.



Predota, Chialvo, Cummings; Fig 1.



Predota, Chialvo, Cummings; Fig 2.



Predota, Chialvo, Cummings; Fig 3.